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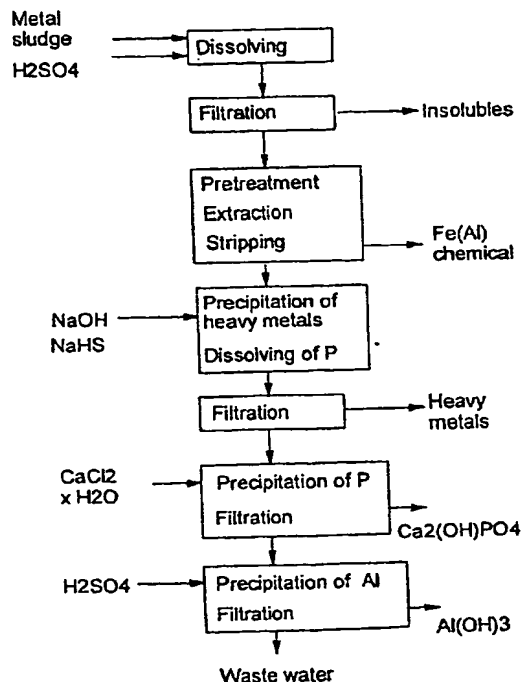
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(54) Title: TREATMENT METHOD FOR WASTE WATER SLUDGE COMPRISING AT LEAST ONE METAL

(57) Abstract

A method for treating waste water sludge comprising at least one metal originating from a waste water treatment coagulant, and phosphorus and heavy metals in order to recover said at least one metal and phosphorus and to discharge said heavy metals, said method comprising: acidifying said waste water sludge to dissolve metals contained in the sludge; subjecting the acidified waste water sludge to liquid-liquid extraction for recovering at least a portion of said at least one metal; treating the raffinate of the extraction in a first precipitation stage with appropriate chemicals for precipitating heavy metals, and thereafter discharging the precipitate thereby leaving a solution having a decreased content of heavy metals; and treating the solution having a decreased content of heavy metals in a second precipitation stage with appropriate chemicals for precipitating phosphorus and thereafter recovering the precipitated phosphorus.



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Treatment method for waste water sludge comprising at least one metal.

The invention relates to a method for treating waste water sludge comprising at least one metal, especially iron and possibly aluminium, originating from a waste water treatment coagulant, and phosphorus and heavy metals in order to recover said at least one metal and phosphorus and to discharge said heavy metals. In particular, the sludge is from a waste water purification process where waste water is chemically precipitated using coagulants containing iron and possibly aluminium.

Disposal of waste water sludge is a major problem in water purification plants. This is partly due to the heavy metal content of the sludge. It is difficult to find suitable places for the waste and as standards rise landfilling is becoming more and more expensive. From this perspective the idea of recycling the waste water sludge is becoming increasingly important. A complete recycling of waste water sludge would involve recycling of coagulants (iron and aluminium), part of the organic substances of the sludge, recovery of phosphorus, and separation of the heavy metals from the sludge. Until now recycling of the sludge has been realized only partially. There are no existing production methods for separating coagulant chemicals and phosphorus from the sludge.

Sludge comes from various sources of the waste water purification process i.e. from pre-precipitation, simultaneous precipitation and post-precipitation stages. One possible treatment procedure for the sludge is first to dewater it to a dry solids content of 15-25% and then to use in agriculture, compost, incinerate or transport the dewatered sludge to a dump.

Another possible procedure is to acidify the precipitation sludge to dissolve metals. Insoluble substances are removed by filtering. The dissolved metals and phosphorus in the

filtrate are precipitated and a sludge, which will be called a metal sludge, is obtained. The metal sludge contains the iron and aluminium of the used coagulant and, in addition, phosphorus and heavy metals. The procedure can also be performed at an elevated temperature to improve yield and filterability i.e. the dewatering properties of the sludge. The sludge to be treated can be a pre-precipitation sludge, a simultaneous precipitation sludge, post-precipitation sludge or a mixture thereof.

One additional alternative for treating the sludge is hydrolysis where the purpose is to hydrolyse organic material of the sludge into short-chained compounds to be utilized in later stages of the waste water treatment process, especially as carbon source in the denitrification stage. During hydrolysis, the metals of the raw sludge dissolve in the hydrolysate solution. In the so-called thermal acid hydrolysis the temperature is 150-160°C and pH<2 preferably 1-1.5. After the hydrolysis, the insoluble part i.e. the organic sludge is separated, the sludge containing mainly insoluble organic and partly inorganic material e.g. fibres and silicate minerals. The pH of the obtained solution is raised above the neutral level using a base so that the dissolved metals precipitate as hydroxides and phosphates. The precipitated sludge i.e. the metal sludge is then separated. The metal sludge contains iron and aluminium and also phosphorus and heavy metals.

Acidification nor hydrolysis of sludge is not commonly used in waste water purification. One reason is poor profitability. An additional problem is the metal sludge which has no use. The metal sludge contains heavy metals which makes the sludge a harmful waste for the environment.

The metal sludge can be dissolved in sulphuric acid or possibly in hydrochloric acid and the insoluble substances can be filtered. The acidic filtrate solution contains the coagulants, phosphorus and heavy metals. It cannot be

recycled or utilized in any other way as such and there are no existing methods to separate the elements.

Solvent extraction i.e. liquid-liquid extraction is a well-known method for separating different elements from each other and, in principle, it could be used to separate said elements. However, there are difficulties in applying extraction to the acidified metal sludge of the above kind or to any other acidified waste water sludge. The acidic solution obtained by leaching waste water sludge with sulphuric acid not only contains dissolved metals but also insoluble fine solid particles, colloidal components, humic acids etc. These impurities comprise an undesirable organic residue (crud) which has the most unfavourable effect on extraction. It significantly retards mass transfer and phases disengagement. In disengagement of phases, after contacting the organic and aqueous phases, this substance usually collects as a separate layer between the phases. Therefore, the existence of the insoluble residue has prevented extraction methods from being exploited in the recovery of iron and aluminium from acidified sewage sludge.

Cornwell and Zoltek (J. Water Pollut. Control Fed., Vol 49, p. 600-612) have presented an extraction method for the recovery of aluminium from a sludge containing aluminium as aluminium hydroxide. The extraction solvent is a mixture of monoethyl hexyl phosphate (MEHPA) and di-(2-ethyl hexyl) phosphate (DEHPA). A process employing solvent extraction with organic extractants for the removal of iron from aqueous acidic solutions has been suggested in the patent publication EP 58148. The objective of the method was to recover pure acid by extracting iron ions into organic solvent. Solvent extraction used for the selective recovery of dissolved iron and aluminium can, with a proper solvent, efficiently separate iron and aluminium from heavy metals.

The objective of this invention is to provide a method whereby the sludge problem in a waste water purification

- plant can be solved. The main objective is to provide a method whereby iron, aluminium and phosphorus of a metal sludge can be recovered. Iron and aluminium can be recycled in the purification process, phosphorus can be used e.g. as
- 5 a fertilizer and, at the same time, the sludge containing the heavy metals can be separated and more easily disposed. This objective can be accomplished by the present invention, and thus the present invention provides a method for treating waste water sludge comprising at least one metal
- 10 originating from a waste water treatment coagulant, and phosphorus and heavy metals in order to recover said at least one metal and phosphorus and to discharge said heavy metals, said method comprising:
- acidifying said waste water sludge to dissolve metals con-
- 15 tained in the sludge;
- subjecting the acidified waste water sludge to liquid-liquid extraction for recovering at least a portion of said at least one metal;
- treating the raffinate of the extraction in a first precipi-
- 20 tation stage with appropriate chemicals for precipitating heavy metals, and thereafter discharging the precipitate thereby leaving a solution having a decreased content of heavy metals; and
- treating the solution having a decreased content of heavy
- 25 metals in a second precipitation stage with appropriate chemicals for precipitating phosphorus and thereafter recovering the precipitated phosphorus.
- Preferably the waste water sludge to be treated with the
- 30 method of the present invention comprises metal sludge obtained by subjecting waste water sludge from a waste water treatment plant to acid treatment followed by precipitation of metal sludge from the filtrate.
- 35 The method of the invention is a significant improvement compared to the conventional practice in the field and offers a sustainable solution for the utilization of waste water sludge. The invention renders utilization of the

precipitated metal sludge possible. Phosphates and raw material for coagulant chemicals can be produced from the metal sludge. Furthermore, heavy metals can be separated whereby they do not harm the environment. The method
5 improves profitability of sludge acidification or hydrolysis. In the method of the invention, Fe and Al are recovered as a solution which can be used in coagulation. Phosphorus is precipitated as calcium phosphate or magnesium ammonium phosphate, for example, which can be used in
10 fertilizers.

Heavy metals of the metal sludge are separated by precipitation. The amount of the precipitated sludge containing heavy metals is small so that dumping of the
15 sludge is easier and does not cause any harm to environment.

According to the invention the acidified sludge solution can be treated with an oxidizer like a strong solution of hydrogen peroxide prior to the liquid-liquid extraction
20 stage to transform the organic substances of the sludge solution into such a form that does not have an unfavourable effect on the extraction and to oxidize the bivalent iron of the sludge solution into a trivalent iron. When hydrogen peroxide is added into a sludge with bivalent iron and
25 organic compounds, a so-called Fenton-reagent is formed. This means that bivalent iron and hydrogen peroxide form hydroxyl radicals which function as very strong oxidizer being able to tackle the organic compounds with the desired effect. Other alternative oxidizers are oxygen, ozone,
30 potassium permanganate, solution of potassium dichromate, chlorine, and chlorine dioxide. After this treatment the solution can be filtered and the filtrate solution is then taken to the liquid-liquid extraction stage.

35 According to the invention, it is also possible to remove organic material so that the waste water sludge is calcined before acidification at a temperature of 300°C or over whereat organic material burns out. The calcination is to be

performed in an atmosphere with an excess of oxygen. In this case oxidation is not needed.

The liquid-liquid extraction stage comprises an extraction stage and a stripping stage. In the extraction stage, said acidified waste water sludge is brought into contact with an extraction solution which is immiscible with water for forming an aqueous phase i.e. raffinate and an organic phase which organic phase contains ions of said metal. The raffinate is separated from the organic phase. In the stripping stage, the organic phase is brought into contact with an acidic aqueous stripping solution for forming an aqueous phase and an organic phase. The aqueous phase containing the desired metal ions is separated from the organic phase.

The extraction solution contains an organic phosphate, an organic solvent and possibly a long-chained alcohol. The organic phosphate is advantageously an alkyl phosphate like a monoalkyl phosphate e.g. a mono-(2-ethyl hexyl) phosphate (MEHPA), dialkyl phosphate e.g. di-(2-ethyl hexyl) phosphate (DEHPA) or trialkyl phosphate e.g. tributyl phosphate, or a mixture thereof e.g. a mixture of MEHPA and DEHPA (MDEHPA). The organic solvent is advantageously a long-chained hydrocarbon solvent like kerosene. The long-chained alcohol can be 2-octanol, for example.

The stripping solution advantageously consists of hydrochloric acid or sulphuric acid. Stripping can also be performed in reducing conditions which can be accomplished by using a stripping solution containing sulphuric acid obtained by bubbling sulphur dioxide in water or dilute sulphuric acid.

According to the invention it is possible to subject the raffinate of the extraction prior to the first precipitation to a treatment with an alkali hydroxide for precipitating a further portion of iron and possibly aluminium as

phosphates, and thereafter separating the phosphate precipitate. The alkali hydroxide, e.g. sodium hydroxide, is preferably added in an amount to raise the pH to a value between 2 and 4. The separated phosphate precipitate can be

5 treated with an alkali hydroxide, e.g. sodium hydroxide, thereby forming insoluble iron hydroxide and a solution comprising soluble alkali phosphate and possibly aluminium hydroxide. Said solution can be introduced into the first or second precipitation stage.

10

According to the invention, the acidic raffinate is treated in the first precipitation stage with a heavy metal binder, like hydrogen sulphide or sulphide, e.g. sodium sulphide or sodium hydrogen sulphide or ferrous sulphide, at a suitable

15 pH value for precipitating heavy metals and iron and at which pH aluminium can precipitate as a hydroxide or a phosphate. The precipitate is separated and the obtained aqueous solution is treated in a second precipitation stage with a reagent precipitating phosphorus, like calcium or

20 magnesium oxide, calcium or magnesium hydroxide or calcium or magnesium chloride, at a suitable pH value for precipitating phosphorus as phosphates, like calcium or magnesium phosphate. In the presence of ammonia, the phosphorus can be precipitated specifically as $MgNH_4PO_4$ (MAP). This

25 provides a means to remove ammonia from the solution. Part of the Mg used in this precipitation can also originate from the waste water sludge.

The method according to the invention can further comprise

30 a third precipitation stage wherein aluminium is precipitated as aluminium hydroxide.

According to an advantageous embodiment the acidic raffinate is treated in the first precipitation stage with sodium

35 sulphide adjusting the pH to a value within 5-8, using sodium hydroxide, MgO or $Mg(OH)_2$, or ammonia, for precipitating heavy metals and iron, which has come through the extraction stage, and possibly aluminium. The precipitate is

separated and the aqueous solution obtained is treated in the second precipitation stage with a calcium or magnesium compound like calcium chloride, magnesium oxide, magnesium hydroxide or magnesium chloride possibly adjusting the pH value for precipitating calcium phosphate or magnesium ammonium phosphate, and the precipitate obtained is separated.

According to another advantageous embodiment of the invention, the acidic raffinate is treated in the first precipitation stage with a S^{2-} or HS^- containing reagent and, at the same time with the sulphide addition, raising the pH to a value of about 6-7, using a base like sodium hydroxide, for precipitating heavy metals and iron and possibly aluminium. Then the pH is adjusted to a value of over 9, preferably about 12 using sodium hydroxide, whereby the possibly precipitated aluminium is redissolved. The precipitate containing heavy metals is then separated. The aqueous solution containing phosphorus and aluminium is treated in the second precipitation stage with calcium chloride for precipitating calcium phosphate. The precipitate obtained is separated. The aqueous solution containing aluminium is treated in the third precipitation stage with an acidic compound like e.g. sulphuric acid for precipitating aluminium hydroxide and the precipitate obtained is separated.

A modification to the above embodiment, which is particularly suitable for removing possible Cr from the raffinate, is as follows. In the first precipitation stage, the pH of the acidic raffinate is adjusted to a value of about 3-4, using sodium hydroxide, and then the raffinate is treated with sodium sulphide for precipitating some of the heavy metals and iron residuals and possibly minor amounts of aluminium. The precipitate, which also contains Cr as chromium phosphate, is separated, after which pH is adjusted to a value of about 12 and over using sodium hydroxide. The precipitate possibly formed is separated. This precipitate

contains also heavy metals. The aqueous solution containing Al and PO_4 is treated in the second precipitation stage with calcium chloride for precipitating calcium phosphate. The precipitate is separated and the aqueous solution obtained
5 is treated in the third precipitation stage with sulphuric acid for precipitating aluminium hydroxide and the precipitate obtained is separated. The two precipitates containing heavy metals are united for disposal.

10 The method of the invention partly solves the sludge problem in a waste water purification plant by improving usability of the solid sludge of the waste water purification process. This is due to several factors. First, the amount of solid material decreases. There are less heavy metals in the
15 sludge whereby it has better possibilities to be used in agricultural applications and incineration is safer. The calorific power of the dry solids is higher and the amount of remaining ash is lower. In addition, the heavy metal content of the ash is lower. Since the precipitated sludge
20 which contains the heavy metals has a relatively small volume, it can be disposed of in a controlled manner without any harm to the environment.

The invention is described in more details in the following
25 referring to the enclosed drawings in which

figure 1 shows an acidification process of precipitated sludge as a block diagram,
figure 2 shows a method according to the invention for
30 treating a metal sludge obtained from a waste water sludge as a block diagram,
figure 3 shows a second treatment method according to the invention,
figure 4 shows a third treatment method according to the
35 invention and
figure 5 shows a fourth treatment method according to the invention.

Figure 1 shows diagrammatically processing of a sludge from a water treatment plant. The metals in the sludge dissolve in the solution during acidification. The insoluble part i.e. the organic sludge is separated, the organic sludge containing primarily fibres and possibly insoluble silicate minerals. For neutralizing the solution and precipitation of metals e.g. lime is added to the solution. In the separation stage subsequent to the neutralization stage, the metal sludge is separated. The filtrate is led to later stages of the waste water treatment process.

According to Figure 2 the metal sludge is dissolved in sulphuric acid or possibly in hydrochloric acid in the dissolving stage and insoluble substances are separated by filtering in the filtration stage.

The solution obtained from the filtration (filtrate) is led to the extraction stage. For example, following contents have been analyzed from the acidic solution: Fe (max. 6%) both ferric and ferrous, aluminium (max. 1%), Ca (max. 1000 ppm), Mg (max. 100 ppm), Pb (max. 100 ppm), Cu, Ti, Cd, etc. The contents of metals in the solution may vary if Al has been used as the coagulant. The content varies also depending on what neutralizing base has been used in the precipitation of the original metal sludge. The extractant is a mixture of two or more organic compounds where the diluent for the effective agent like alkyl phosphate is a straight-chain hydrocarbon like kerosene and, if necessary, an additional compound like a long straight-chain alcohol for enhancing the phases disengagement. Before the extraction stage the solution can be treated with an oxidizing agent which oxidizes iron into Fe^{3+} and oxidizes organic substances into such form that they do not hinder extraction. Strong H_2O_2 can be preferably used as the oxidizing agent. It is also possible that the oxidizing agent is added before the filtration stage.

In the extraction stage the acid solution is contacted with the above mentioned organic solution whereupon trivalent iron and partly also aluminium are transferred from the acid solution into the organic solution. Extraction is preferably performed at constant pH since extraction efficiency decreases with decreasing pH. pH can be adjusted by using alkali hydroxide or ammonia water, for example. After extraction, the organic phase and the aqueous phase are separated and the obtained extract solution containing the iron and aluminium is contacted with strong hydrochloric acid, for example, whereby trivalent iron and aluminium are transferred again to the acidic solution. This re-extraction or stripping can be also performed by using sulphuric acid whereby trivalent iron is reduced to divalent form which has less tendency to remain in the organic solution. The organic solvent, which is free of metals, can be recycled back to the process. The acidic solution obtained from the re-extraction i.e. the raffinate of stripping contains iron and aluminium and can be further used for production of coagulants. Generally, the mixer/settler apparatus contains several equilibrium stages with counter- or cross-flow of phases.

The acid solution (pH 0.5-1) obtained from the extraction stage or the raffinate of extraction contains mainly phosphorus but also some unextracted iron, aluminium and heavy metals. This raffinate must be purified from organic residues e.g. by using active carbon before any further treatment.

According to Figure 2, sulphides like NaHS, Na₂S, FeS or H₂S are added to the solution for precipitation of metals. Other known heavy metal binders can also be used. The pH of the solution is adjusted to the range of about 3-4 to enable precipitation. NaOH can be used for the pH adjustment, for example. Since each heavy metal precipitates at a specific pH, addition of sulphides is done simultaneously with raising of pH from 3-4 to 6-7 to allow precipitation of all

the heavy metal components. The iron and aluminium which remain from the extraction stage precipitate as phosphates together with heavy metals which precipitate as sulphides, and/or hydroxides, and/or phosphates. After precipitation, 5 pH is raised to over 9, preferably to about 12, by adding NaOH so that the only soluble components which remain in the solution are aluminium and phosphorus whereas other metals remain in insoluble form. In other words, the Al-phosphate which precipitated in the earlier stage dissolves as pH is 10 raised.

In the filtration stage, which follows the precipitation of heavy metals, the precipitate is separated from the liquid phase containing then primarily phosphate and sodium 15 aluminate. The last residue of iron are separated at this stage along with the precipitate.

In the phosphorus precipitation stage, CaCl_2 is added to the filtrated solution to precipitate phosphorus as calcium 20 phosphate which is filtrated in the subsequent filtration stage. The remaining filtrate contains soluble aluminium which is precipitated as aluminium hydroxide by lowering the pH of the solution to level 7-8 using H_2SO_4 , for example.

25 According to a second method, which is presented in Figure 3, precipitation of heavy metals is performed at pH of about 5-8 using Na_2S and NH_4OH for the pH adjustment. Heavy metals and unextracted Fe and Al precipitate as sulphides and phosphates. The precipitate is separated after which Mg is 30 added as MgCl_2 , MgO or $\text{Mg}(\text{OH})_2$, and pH is raised if necessary to level 8-9 using NH_4OH . Phosphorus in the solution precipitates as MgNH_4PO_4 , which can be used as a raw material for fertilizers. The amount Mg and NH_4 chemicals mentioned 35 above is proportioned so that they are in stoichiometric ratio with the amount of PO_4 to be precipitated. Preferably there is a small surplus of Mg.

According to another embodiment of the method of the invention heavy metal precipitation is performed at pH of about 4 using Na_2S and NH_4OH for the pH adjustment. Heavy metals precipitate as sulphides and/or hydroxides and/or phosphates. Next, MgO is added to the solution and pH is raised to 5-6 whereby aluminium and chromium precipitate as phosphate and/or hydroxide. The precipitate is separated whereafter MgO and NH_4OH are further added to the solution so that pH is about 9 whereby phosphorus precipitates as MgNH_4PO_4 .

A possible procedure is that first the heavy metals are precipitated at pH 4 in the above described way whereafter aluminium and chromium are precipitated at pH 5-6 and then filtration is performed.

After the extraction/stripping stage the raffinate solution always contains some Fe and Al (see Table 2 in Example 5) which bind an equal number of moles of phosphorus. For example, the amount of Fe given in Table 2 in Example 5 binds an excessive amount of P of the raffinate solution. Therefore, Fe and Al must be removed. If the pH of the solution is raised FePO_4 and AlPO_4 will precipitate and the phosphorus is lost. There are several different ways to handle the problem of remaining Fe and Al in the raffinate solution.

The first method is presented in Fig. 2. After the extraction/stripping stage, the remaining Fe and Al will be first precipitated as phosphates along with the heavy metals. Upon raising the pH with NaOH to about 12 AlPO_4 will be redissolved. Ferric phosphate, on the other hand, will convert to an insoluble ferric hydroxide, which is removed along with the heavy metal precipitate, and the PO_4^{3-} of the ferric phosphate is dissolved.

The second method is presented in Fig. 3. In this case, the Fe and Al are precipitated together with the heavy metals as

phosphates. Apart from losing the Fe and Al remaining in the raffinate solution, an equal mole number of P is also lost.

A third method for handling the remaining Fe and Al is shown in Fig. 4. In this case, there is an extra precipitation stage after the extraction/stripping. The pH is raised to about 3 with NaOH. The pH can vary in the range 2-4. At this pH, ferric phosphate, FePO_4 , and possibly AlPO_4 will precipitate at a good yield. The precipitate is then separated by filtration. The precipitate can be utilized as such or it can be returned to the dissolution stage. The filtrate solution, free of Fe and Al, is treated in the same way as in the process of Fig. 3. The drawback of this method, in the case the FePO_4 precipitate is returned to dissolution stage, is that the recycling leads to an increase in the P content of the extracting solution. This is not desired. It would be more desirable to return only the Fe of the FePO_4 back to the dissolution stage and lead the PO_4 of the FePO_4 forwards in the process.

20

A fourth method is presented in Fig. 5. In this case the Fe and Al is precipitated as FePO_4 and AlPO_4 , which are separated by filtration. Next, the phosphate precipitate is dissolved with NaOH with a slight warming (60°C) of the solution. Ferric phosphate is dissolved and soluble sodium phosphate and insoluble $\text{Fe}(\text{OH})_3$ is formed. Aluminium phosphate is totally dissolved. After separation, the ferric hydroxide precipitate is returned to the beginning of the process and the sodium phosphate solution, containing aluminium, is led to the subsequent process stage i.e. to the stage where heavy metals are precipitated or even to the stage of phosphate precipitation. Another possible process variant is such that the sodium phosphate is precipitated from the solution and is utilized as such as a detergent phosphate.

35

Instead of returning the ferric hydroxide precipitate to the beginning of the process there is another interesting possibility. The ferric hydroxide let to dry and then it is

added into the raffinate of the stripping stage i.e. to the aqueous phase. The added ferric hydroxide contributes in two different ways: firstly it neutralizes the free acid of raffinate and secondly it raises the relatively low Fe-content of the raffinate solution.

It is worth noting in the process of Fig. 5 that the amount of NaOH used for dissolving the FePO_4 precipitate reduces the amount of NaOH needed at the precipitation of heavy metals. This means that no extra NaOH is needed in the process of Fig. 5 compared to the process of Fig. 4 or Fig. 3. Furthermore, there is no increase in the P content of the extraction solution because phosphorus bound to Fe is not returned to the beginning of the process but the soluble phosphorus is led forwards in the process.

The process of the invention has several alternative modes of operation. One interesting alternative, which greatly improves the recovery of nutrients i.e. phosphorus and ammonia of the waste water, is such that the metal sludge is formed by neutralizing the acidic hydrolysate with a Mg-compound. This has the effect that $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ (struvite) will precipitate into the metal sludge reducing the content of ammonia in the hydrolysate. If Mg-compounds and possibly ammonia are properly used in all pH adjustments of the process so that the number of moles of ammonia equals to the number of moles of phosphorus corresponding to the mole ratio in MgNH_4PO_4 , then after the final precipitation of MgNH_4PO_4 no ammonia will be left and none of it has to be returned to the waste water process. Hence all nutrients have been recovered. If only Mg-compounds have been used in pH adjustments the remaining filtrate solution contains primarily MgSO_4 , which can be separated by evaporation and obtain a product of commercial value.

In the following, the invention will be further explained by means of examples.

EXAMPLE 1.

A solution was obtained by leaching a metal containing waste water sludge with dilute H_2SO_4 and filtering for gypsum removal at approximately pH 1. The density of the solution was 1080 kg/m³ and it contained 0.6% Fe^{2+} , 1.8% Fe^{3+} , 0.21% Al.

H_2O_2 (10 ml) was added to the above solution (120 ml) during 60 minutes in a stirred cell. During feeding H_2O_2 the temperature increased from 20°C to 55°C. The solution was filtered once more through a fuller's earth filter, the bed thickness of which was 10 mm. The filtrate solution (60 ml) was contacted with an organic extraction solvent (180 ml) so that the phase ratio organic/aqueous = 3/1. The organic solvent consisted of 22.5% MDEHPA, 67.5% kerosene and 10% 2-octanol. MDEHPA contained 45% MEHPA and 55% DEHPA. After 20 minutes of mixing the mixture was withdrawn to a separation funnel for phase separation. The organic phase was disengaged from the aqueous phase very rapidly, in 10-15 seconds. Virtually no crud was detected between the phases. The efficiency of the extraction is presented in Table 1a.

Table 1a. Relative amounts of metal components transferred from the aqueous phase to the extractant i.e. the efficiency of extraction (%)

Component	Efficiency
Total Fe	96.4 %
Al	21.3 %

25 ml of the organic extract loaded with Fe and Al was contacted with 6M HCl in a stirred cell for 20 minutes. Thereafter the phases were separated in a separation funnel. The disengagement was again rapid and following stripping efficiencies were obtained (Table 1b):

Table 1b. Relative amounts of metal components transferred from the extractant to the stripping solution i.e. the efficiency of stripping (%)

5	Component	Efficiency
	Total Fe	52.9 %
	Al	70.8 %

10 EXAMPLE 2.

A solution from the extraction stage (207 g) contained 0.12% Fe, 0.18% Al, 1.62% PO_4 and heavy metals: 0.0018% Cu, 0.0009% Cr, 0.0124% Zn. 60 g of NaOH-solution (20%) was added to the solution and the pH rose to 2.7. Then 27.6 g of Na_2S -solution (35%) was added whereby pH rose to 3.8. A precipitate was obtained which contained heavy metals as sulphides. The precipitate was filtered (2.5 g) and analyzed. A qualitative X-ray analysis showed that the precipitate contained following heavy metals: Cu, Pb, As, V, Cr, Sr, Ni.

20 Next, a 57.6 g amount of NaOH (20%) was added to the filtrate (260 g) containing soluble aluminium and phosphorus, among other things, whereupon pH rose to the value of 13. It is typical of aluminium that as pH rises, aluminium first precipitates but begins to redissolve again as pH rises above 8. The aim of raising pH was to redissolve the precipitated aluminium. In this stage, however, hydroxides precipitated from the solution. The precipitate was filtrated and CaCl_2 -solution was added to the filtrate (285 g) and a calcium phosphate precipitate (31.8 g) was obtained which, according to X-ray diffraction, contained $\text{Ca}(\text{OH})_2$ and $\text{Ca}_3(\text{OH})(\text{PO}_4)_3$. The precipitate contained 88 % of the phosphorus of the starting solution i.e the solution obtained from the extraction. Aluminium was also precipitated so that the precipitate contained 45% of the aluminium of the starting solution. The mole ratio $[\text{PO}_4^{3-}]/[\text{Al}]$ was 5.0. In the last stage, H_2SO_4 (10%) was added to the filtrate so that pH sank to value 7. The purpose was to precipitate the

aluminium remaining in the solution. However, no precipitation occurred because aluminium had already precipitated in the previous stages. The original sludge was obtained by an iron coagulant so that amount of aluminium was small.

EXAMPLE 3.

In this example NH_4OH was used for pH adjustment. Precipitation of heavy metals was performed at pH 4.0 using Na_2S -solution. The heavy metal precipitate contained 4% of the original phosphorus and 4% of the original aluminium. Next, pH was raised to level 5.4. The precipitate contained 24% of the original phosphorus and 63% of the original aluminium. After precipitation, MgO and NH_4OH were added to the solution and pH rose to 9.0. A MgNH_4PO_4 -precipitate (struvite) was obtained with about 70% of the original phosphorus and about 30% of the original aluminium. The mole ratio $[\text{PO}_4^{3-}]/[\text{Al}]$ was 6.0.

EXAMPLE 4.

In this example the procedure with respect to pH was the same as in the previous example but now there was no filtration after the heavy metal precipitation stage. Instead, the pH was raised to level 5.4 after the heavy metal precipitation. At this pH precipitation of phosphates took place. The precipitate contained 23% of the original phosphorus and 62% of the original aluminium. Adjustment of pH of the solution was performed using NH_4OH . In this test the yield of phosphorus was of the same order of magnitude as in example 3.

EXAMPLE 5.

The raffinate from the extraction/stripping stage had the analysis of Table 2.

Table 2. Analysis of the raffinate.

Element	Concentration
Fe	0.16 %
Fe ³⁺	0.11 %
Al	0.12 %
P	0.42 %
Cu	6.9 ppm
Cr	5.6 ppm
Zn	7.3 ppm

In order to further reduce the content of Fe in the raffinate, an extra precipitation i.e. a polishing precipitation was performed in the following way. The amount of the above raffinate used in the precipitation was 817.5 g (750 ml) with a pH of 0.86. A 159.1 g amount of NaOH (30 %) was used to raise the pH of the raffinate solution to 2.8. After raising pH, a 1.5 g amount of H₂O₂ was added to make sure that all Fe was in trivalent form. The solution was then stirred for 1 h. A light brown precipitate, identified as FePO₄ by X-ray methods, was obtained. The solution was filtrated to separate the precipitate. The amount the dry precipitate was 10.3 g. The precipitate was washed with 83.9 g of distilled water. This washing water was added to the filtrate and the total amount of filtrate including the water was 984.6 g. The analysis of the filtrate obtained is given in Table 3.

Table 3. Analysis of the raffinate after removal of Fe by a polishing precipitation and the relative reduction of the elements.

Element	Concentration	Reduction-%
Fe	0.005 %	96.2
Al	0.049 %	50.8
P	0.05 %	85.7
TOC	0.04 %	-
Cd	< 0.3 ppm	-
Cu	4.9 ppm	14.5
Cr	3.8 ppm	18.3
Ni	4.5 ppm	-
Pb	< 5 ppm	-
Zn	57 ppm	6

Results of this experiment indicate clearly that iron can be removed effectively by an extra precipitation step. The obtained precipitate can be either utilized as such as an additive in a fertilizer or it can be returned to the beginning of the process i.e. to the dissolution stage. If it is returned to the dissolution stage, the phosphorus content of the process solution will gradually rise to an equilibrium value which is the same the value given in Table 2.

EXAMPLE 6.

A 15 g amount of dried FePO_4 -cake (12% P, 24% Fe) precipitated from a raffinate solution was dissolved into 56 g of water and 26 g of NaOH (50%). The pH was adjusted to 12 and the reaction vessel was slightly warmed so that the temperature was 50°C. After 2 hours the precipitate was filtrated and the precipitate was washed with water. The amount of Fe(OH)_3 precipitate obtained was 7.2 g (dry weight) containing 50% Fe and 2.2% P. This result indicates that an almost complete conversion of FePO_4 to Fe(OH)_3 has taken place in terms of the iron content. Therefore, all Fe of the raffinate can be removed and returned to the

beginning of the process. The filtrate contained less than 0.002 % Fe. The yield of P in the filtrate was more than 90%. This portion of the P can be separated to be led to the following process stage.

5

EXAMPLE 7.

A raffinate solution after separation of FePO_4 and returning of P had the analysis of Table 4 (column A). To precipitate heavy metals from this solution, NaHS and NaOH were added. The precipitate was filtrated and washed with water. The filtrate solution was analyzed for the heavy metals and the results are given in Table 5 (column A). Since the concentrations of the original raffinate were so low, below the detection limit of the elements, these results were not very reliable in showing the efficiency of sulphide precipitation in removing the heavy metals. Therefore, another test was made with the same raffinate but with added heavy metals. The heavy metal concentrations of the raffinate, after the addition, are given in Table 4 (column B).

20

Table 4. Analysis of the raffinate after removal of Fe and return of P. A = original raffinate, B= after addition of heavy metals.

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Element	Concentration A	Concentration B
Fe	0.005 %	
Al	0.049 %	
P	0.39 %	
TOC	0.04 %	
Cd	< 0.3 ppm	20 ppm
Cu	4.9 ppm	24.9 ppm
Cr	3.8 ppm	23.8 ppm
Ni	4.5 ppm	24.5 ppm
Pb	< 5 ppm	25 ppm
Zn	57 ppm	117 ppm

30

35

To an amount of 220.6 g of the above solution, 370 mg NaHS (40%) and 9.0 g NaOH (30%) were added to precipitate heavy metals as sulphides. The pH rose to 8.5. The precipitates were filtrated and washed with 51.2 g of water. The dry weight of the heavy metal cake was 1.725 g. The amount of filtrate solution (including the wash water) 261 g. The heavy metal concentrations of the filtrate and the corresponding reduction percentages are given in Table 5 (column B).

10

Table 5. Analysis of the raffinate solution after precipitation of heavy metals, the right column gives the relative reduction of the concentration of the elements.

Ele- ment	Concentration A	Concentration B	Reduction B
P	0.27 %	-	-
Mg	0.036 %	-	-
NH4	0.04 %	-	-
Al	<0.004 %	-	-
Cd	< 0.3 ppm	< 1.2 ppm	> 94 %
Cu	< 2 ppm	< 2.4 ppm	> 90 %
Cr	< 3 ppm	< 3.6 ppm	> 85 %
Ni	< 2 ppm	< 2.6 ppm	> 91 %
Pb	< 5 ppm	< 5 ppm	> 76 %
Zn	0.3 ppm	0.38	> 99 %

Results of Table 5 shows that heavy metals can be effectively removed from the raffinate solution by sulphide precipitation. There is some loss in phosphorus. This is partly due to aluminium which binds phosphorus at this pH and partly formation of magnesium phosphate.

35 EXAMPLE 8.

Table 6 presents results from tests for precipitating heavy metals at various pH. The differences in the results are

small. If pH goes over 6 there is a danger that MgNH_4PO_4 starts to precipitate leading to phosphorus losses in the raffinate.

- 5 Table 6. Analysis of the original raffinate solution before precipitation of heavy metals and after precipitation at various pH.

Element	Original	Filtrate after precipitation		
		pH 5.1	pH 6.0	pH 6.6
Cr (ppm)	4.2	< 2	< 2	< 2
Ni (ppm)	5.4	2.4	< 2	< 2
Zn (ppm)	60	< 0.3	< 0.3	< 0.3
P (%)	-	0.35	0.36	0.34

EXAMPLE 9.

To an amount of 250 g of the filtrate solution from example 7, 5.32 g of MgCl_2 and 4 g of NH_3 -solution (25%) were added to precipitate P as MgNH_4PO_4 . The pH was adjusted to 9. The solution was filtrated yielding a cake with a dry weight of 3.55 g. The cake was analyzed by XRD and was identified as $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ (struvite). The cake was dried to a dry weight of 3.55 g and analyzed. The dried cake contained 14% Mg, 4.5% NH_4 , and 20.8% P. The crystal water and half of the ammonia had evaporated during drying due to a too high temperature. The yield of P in this precipitation was 96.3%. The filtrate solution (246.5 g) contained < 0.01 % P.

EXAMPLE 10.

A 118 g amount of the filtrate, from which heavy metals had been removed by sulphide precipitation and which contained 0.23% P, was taken and pH was adjusted from 8.0 to 6.0 with 96% H_2SO_4 . A 1.93 g amount of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ was then added and the batch was mixed for 2 hours, the temperature being about 50°C. The pH of the batch was then raised from 5.3 to 8.5 by adding 0.63 g Ca(OH)_2 . After mixing for 2 h, the batch was

filtrated yielding a cake with a dry weight of 2.55 g and a 106.5 amount of filtrate. The cake was analyzed by XRD and was identified as $\text{Ca}_3(\text{OH})(\text{PO}_4)_3$. It contained 12% P and 29% Ca. The filtrate contained < 0.01% P.

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EXAMPLE 11.

A metal sludge with DS of 29.6% was calcined at 325°C for 1 h. The ignition loss was 26.8%. The calcinate containing 17% Fe, 3.2% P, 5.5% Al was then dissolved in sulphuric acid (96%) for 2 h at a temperature of over 100°C. The solution was filtrated and the filtrate contained 4.6% Fe, 0.38% Al, 0.86% P, and 0.05% TOC. In the extraction stage there was no crud formation and the extraction rate was high. Extraction efficiency was of the same order as in parallel extraction tests with the hydrogen peroxide pre-treatment without any calcination.

The invention is not limited to the above examples but can be varied within the limits of the enclosed claims. Therefore, dissolution of metals from waste water sludge can be performed without thermal treatment. Thermal treatment is advantageous since it improves filterability of the organic sludge and solvability of metals. It is essential for the implementation of the method of the invention that the metals in the waste water sludge are first dissolved through acidification and then precipitated as phosphates and hydroxides.

Claims

1. A method for treating waste water sludge comprising at least one metal originating from a waste water treatment coagulant, and phosphorus and heavy metals in order to re-
5 recover said at least one metal and phosphorus and to discharge said heavy metals, characterized in that the method comprises:
acidifying said waste water sludge to dissolve metals contained in the sludge;
10 subjecting the acidified waste water sludge to liquid-liquid extraction for recovering at least a portion of said at least one metal;
treating the raffinate of the extraction in a first precipitation stage with appropriate chemicals for precipitating
15 heavy metals, and thereafter discharging the precipitate thereby leaving a solution having a decreased content of heavy metals; and
treating the solution having a decreased content of heavy metals in a second precipitation stage with appropriate chemicals for precipitating phosphorus and thereafter recovering
20 the precipitated phosphorus.
2. A method of claim 1, wherein said at least one metal to be recovered comprises iron and aluminium or iron.
25
3. A method of claim 1 further comprising subjecting said waste water sludge prior to the liquid-liquid extraction to a treatment with an oxidizer, such as a strong hydrogen peroxide solution, to convert organic material contained in the
30 sludge into a form that does not have an unfavourable effect on the liquid-liquid extraction, and to oxidize divalent iron contained in the sludge to trivalent iron.
4. A method of claim 1 further comprising subjecting said
35 waste water sludge prior to acidification to calcination for incineration of organic material contained in the sludge.

5. A method of claim 1, wherein said liquid-liquid extraction comprises an extraction stage and a stripping stage, wherein said acidified waste water sludge is contacted in the extraction stage with a water immiscible extraction solution thereby forming an aqueous phase i.e. raffinate and an organic phase loaded with ions of said at least one metal, the raffinate is separated from the organic phase, the organic phase is contacted in the stripping stage with an acidic aqueous stripping solution thereby forming an aqueous phase loaded with ions of said at least one metal and an organic phase, and the aqueous phase loaded with the desired metal ions is separated from the organic phase.
6. A method of claim 5, wherein said extraction solution comprises an organic phosphate such as an alkyl phosphate, and an organic solvent.
7. A method of claim 6, wherein said alkyl phosphate is selected from the group consisting of monoalkyl phosphates, such as mono-(2-ethylhexyl)phosphate, dialkyl phosphates, such as di-(2-ethylhexyl)phosphate, and trialkyl phosphates, such as tributyl phosphate, and mixtures thereof, and wherein said organic solvent comprises a long-chained hydrocarbon solvent, such as kerosene.
8. A method of claim 6, wherein said extraction solution additionally comprises a long-chained alcohol, such as 2-octanol.
9. A method of claim 1 or 2 further comprising subjecting the raffinate of the extraction prior to the first precipitation to a treatment with an alkali hydroxide for precipitating a further portion of iron and possibly aluminium as phosphates, and thereafter separating the phosphate precipitate.
10. A method of claim 9, wherein the alkali hydroxide is added in an amount to raise the pH to a value between 2 and

4, and wherein the alkali hydroxide comprises sodium hydroxide.

11. A method of claim 9 or 10, wherein the separated phosphate precipitate is treated with an alkali hydroxide thereby forming insoluble iron hydroxide and a solution comprising soluble alkali phosphate and possibly aluminium hydroxide.

12. A method of claim 11, wherein said solution is introduced into the first or second precipitation stage.

13. A method of claim 1 or 9, wherein the raffinate is treated in the first precipitation stage with a heavy metal binder, such as hydrogen sulphide or a sulphide, e.g. sodium sulphide, sodium hydrogen sulphide or ferrous sulphide, at a suitable pH value for precipitating heavy metals and a further portion of iron, if present, and possibly aluminium, if present, the precipitate is separated and the obtained aqueous solution is treated in the second precipitation stage with a reagent precipitating phosphorus, such as calcium or magnesium oxide, calcium or magnesium hydroxide or calcium or magnesium chloride, at a suitable pH value for precipitating phosphorus as a phosphate, such as calcium or magnesium phosphate.

14. A method of claim 1 further comprising a third precipitation stage wherein aluminium is precipitated as aluminium hydroxide.

15. A method of claim 13, wherein the raffinate is treated in the first precipitation stage with sodium sulphide adjusting the pH to value between 5 and 8 using sodium hydroxide, magnesium oxide, magnesium hydroxide or ammonia for precipitating heavy metals and iron, if present, and possibly aluminium, if present, the precipitate is separated, the obtained aqueous solution is treated in the second precipitation stage with a calcium or magnesium compound,

such as calcium chloride, magnesium oxide, magnesium hydroxide or magnesium chloride, if necessary, adjusting the pH value for precipitating calcium phosphate or magnesium phosphate, and the precipitate is separated.

5

16. A method of claims 13 and 14, wherein the raffinate is treated in the first precipitation stage with hydrogen sulphide or a sulphide, e.g. sodium sulphide, sodium hydrogen sulphide or ferrous sulphide, simultaneously with the addition of hydrogen sulphide or the sulphide raising the pH to a value between 6 and 7 using a base, such as sodium hydroxide, for precipitating heavy metals and iron, if present, and possibly aluminium, whereafter the pH is adjusted to a value over 9, preferably about 12, using sodium hydroxide, whereby the possibly precipitated aluminium redissolves, the precipitate containing heavy metals is separated, the obtained aqueous solution containing phosphorus and aluminium is treated in the second precipitation stage with calcium chloride for precipitating calcium phosphate, the precipitate is separated, the obtained aqueous solution containing aluminium is treated in the third precipitation stage with an acidic compound, such as sulphuric acid, for precipitating aluminium hydroxide, and the precipitate is separated.

17. A method of claims 13 and 14, wherein the raffinate is treated in the first precipitation stage with sodium sulphide adjusting the pH to a value between 3 and 4 using sodium hydroxide for precipitating at least some of the heavy metals and iron, if present, and possibly minor amounts of aluminium, the precipitate is separated, whereafter the pH is adjusted to a value of about 12 or over using sodium hydroxide, the possibly formed precipitate containing heavy metals is separated, the obtained aqueous solution containing aluminium and phosphorus is treated in the second precipitation stage with calcium chloride for precipitating calcium phosphate, the precipitate is separated, and the obtained aqueous solution containing aluminium is treated in the third precipitation stage with an acidic compound, such

a sulphuric acid, for precipitating aluminium hydroxide, and the precipitate is separated.

- 5 18. A method of claim 1, wherein said waste water sludge comprises metal sludge obtained by subjecting waste water sludge from a waste water treatment plant to acid treatment followed by precipitation of metal sludge from the filtrate.

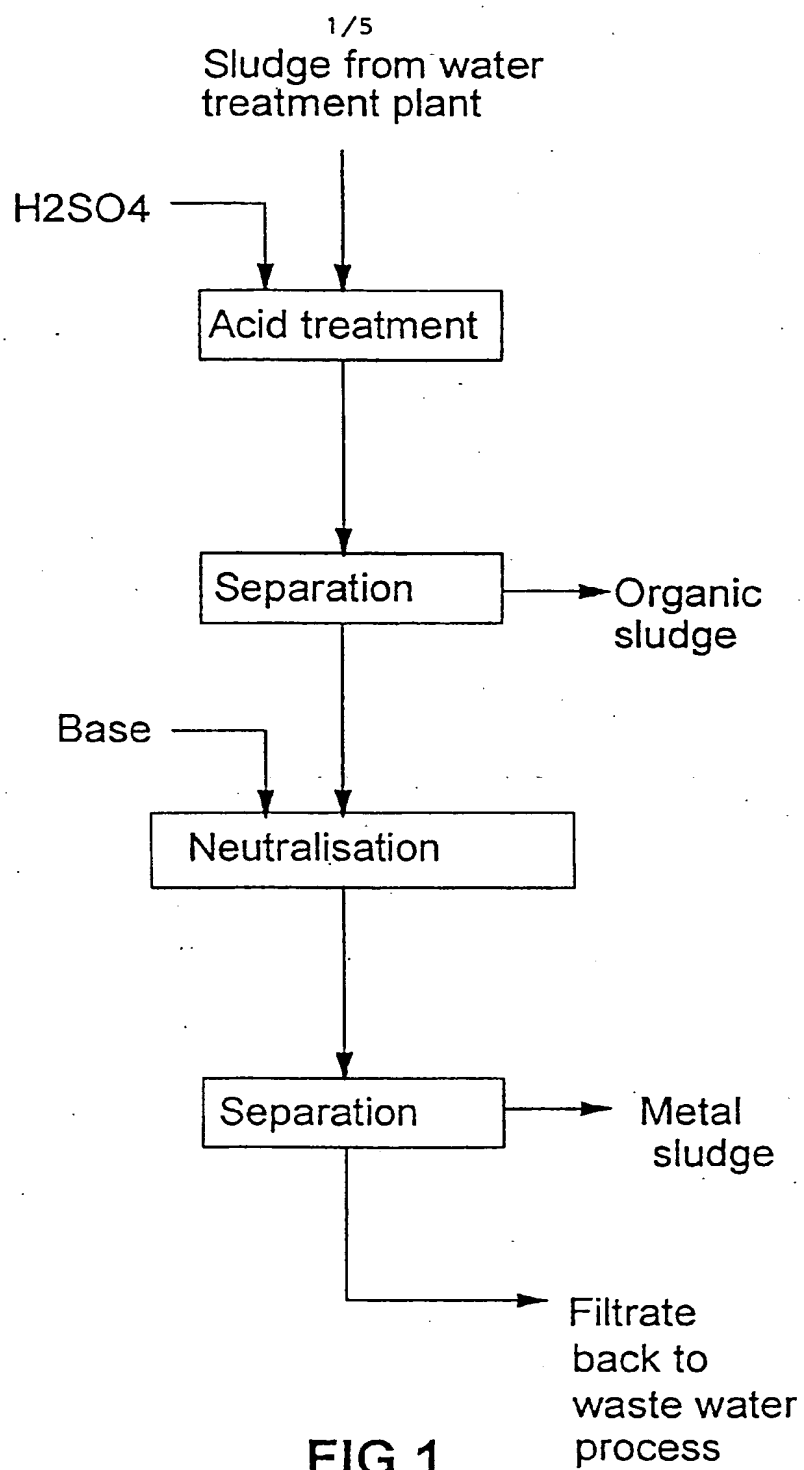


FIG 1

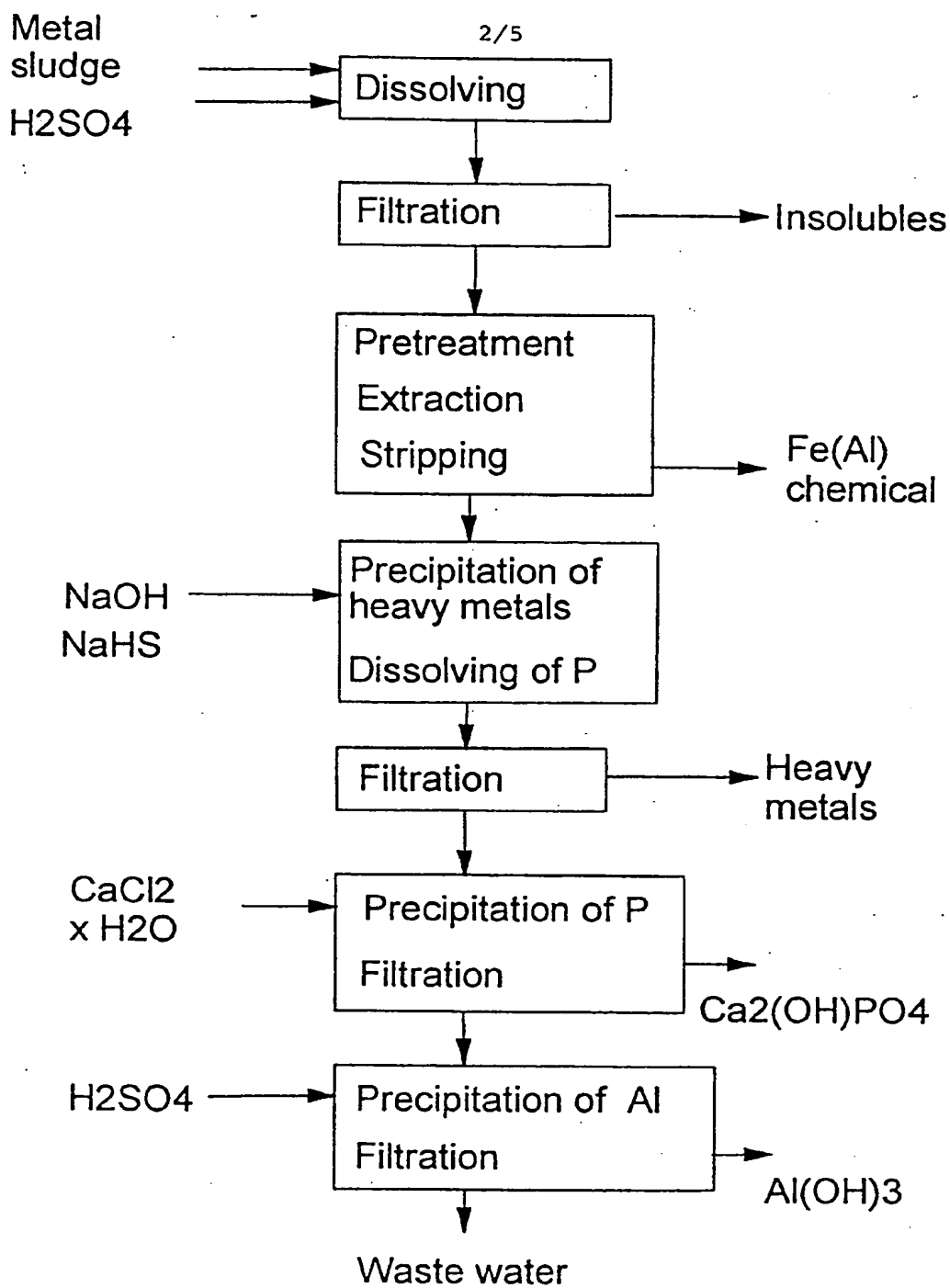
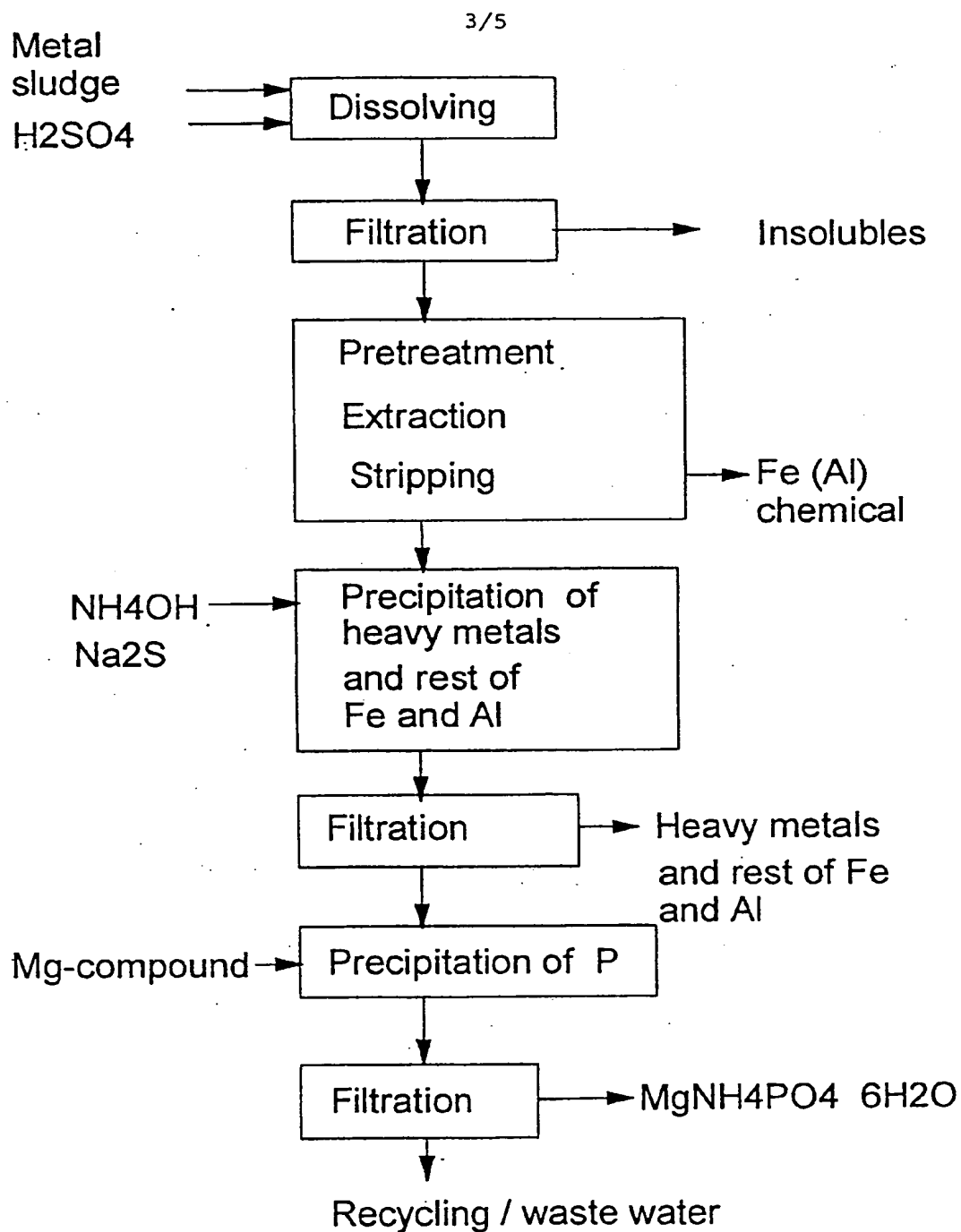


FIG 2

**FIG 3**

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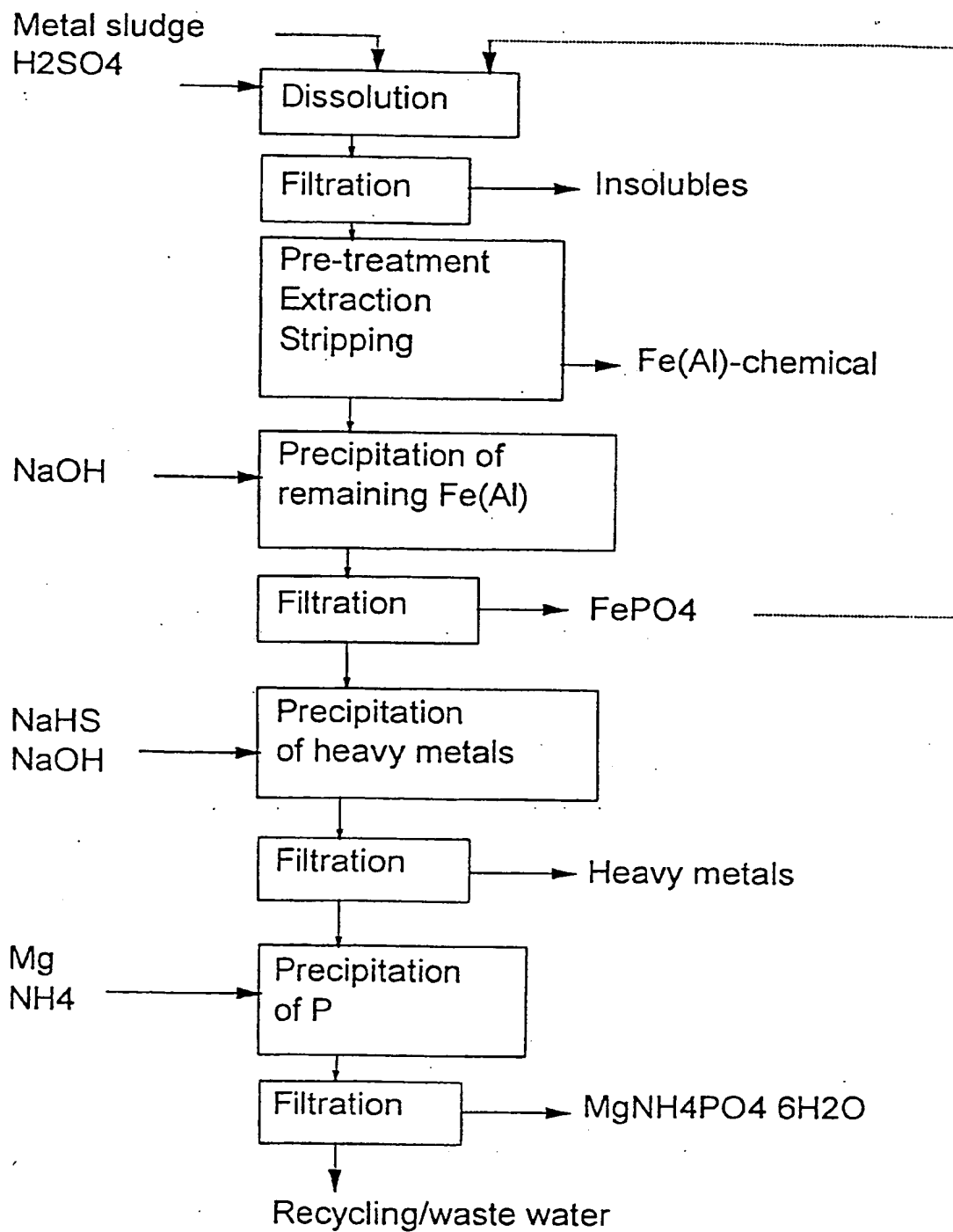


FIG 4

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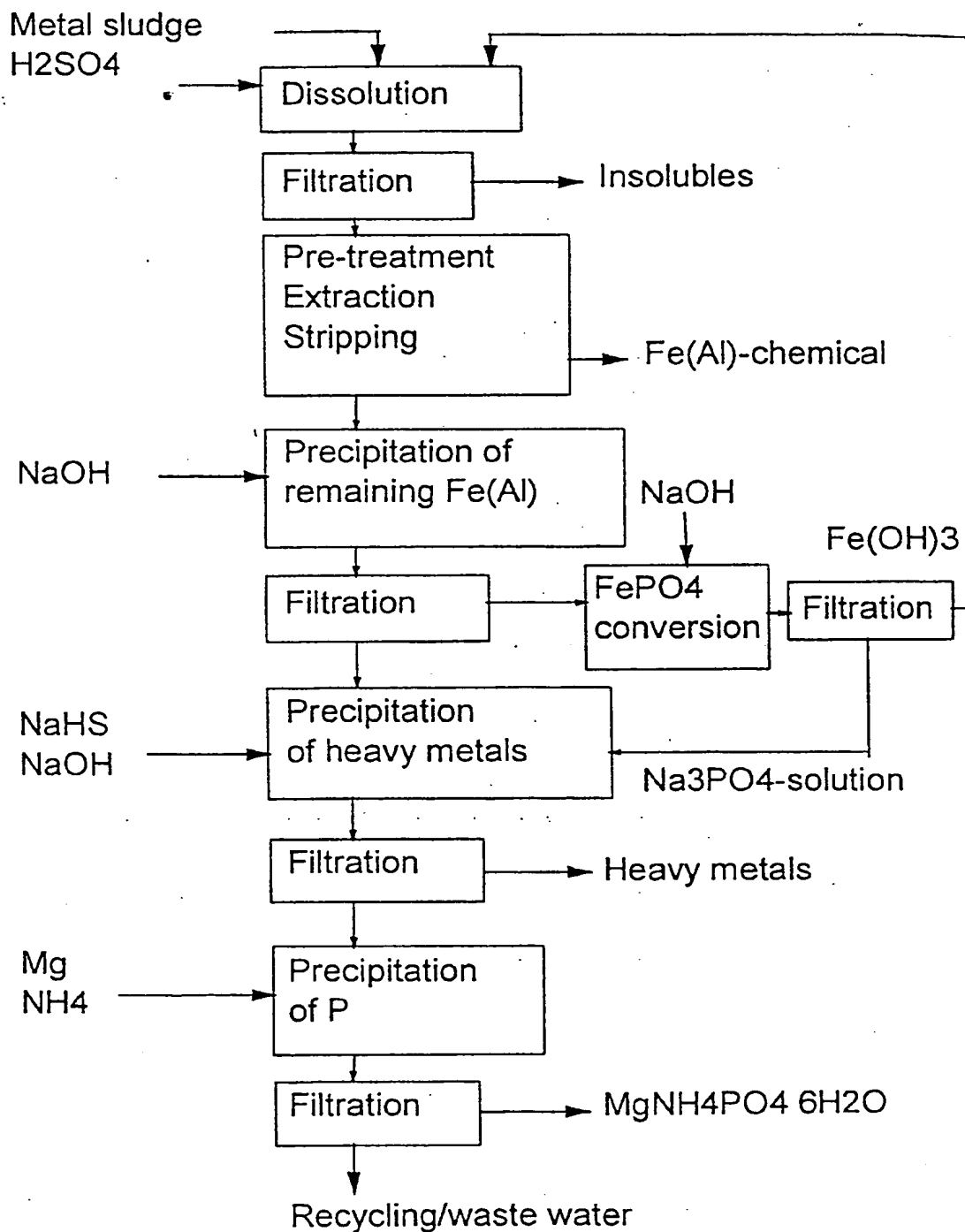


FIG 5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI 94/00376

A. CLASSIFICATION OF SUBJECT MATTER		
IPC6: C02F 1/26, C02F 1/52 According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols)		
IPC6: B01D, C02F		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
SE,DK,FI,NO classes as above		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4954168 (RANKO CRNOJEVICH ET AL), 4 Sept 1990 (04.09.90), claim 1 --	1
Y	US, A, 4284515 (CHONG T. LIU), 18 August 1981 (18.08.81), abstract --	1
A	GB, A, 1595407 (SVENSKA RAYON AKTIEBOLAGET), 12 August 1981 (12.08.81), page 4, line 74 - line 79, claims 1-2 --	1,6,7
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search		Date of mailing of the international search report
28 November 1994		05 -12- 1994
Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86		Authorized officer Bengt Christensson Telephone No. +46 8 782 25 00

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 94/00376

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE, A1, 3005635 (DAMBACH-INDUSTRIEANLAGEN GMBH), 20 August 1981 (20.08.81), claims 1,2 -----	1,13,15,16

INTERNATIONAL SEARCH REPORT
Information on patent family members

29/10/94

International application No.
PCT/FI 94/00376

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 4954168	04/09/90	NONE	
US-A- 4284515	18/08/81	NONE	
GB-A- 1595407	12/08/81	AU-B- 513534	04/12/80
		AU-A- 3510378	18/10/79
		CA-A- 1108320	01/09/81
		DE-A- 2816305	02/11/78
		FR-A,B- 2387069	10/11/78
		JP-A- 54015470	05/02/79
		NL-A- 7803923	17/10/78
		SE-B,C- 405078	20/11/78
		SE-A- 7704357	16/10/78
		US-A- 4151076	24/04/79
DE-A1- 3005635	20/08/81	NONE	